

(This section to be completed by subcontractor requesting document)

Requestor J. Lamb / 1034A
Document Center (is requested to provide the following document)
Date of request 6/14/96 ~~2/2/96~~ Expected receipt of document 7/14/96 ~~3/5/96~~ ~~7/30/96~~
Document number K-904 Date of document 4/21/52
Title and author (if document is unnumbered)

(This section to be completed by Document Center)

Date request received 6/19/96
Date submitted to ADC 7/3/96
Date submitted to HSA Coordinator 6/19/96

(This section to be completed by HSA Coordinator)

Date submitted to CICO 7/3/96
Date received from CICO 7/29/96
Date submitted to ChemRisk/Shonka and DOE 8/1/96

(This section to be completed by ChemRisk/Shonka Research Associates, Inc.)

Date document received _____
Signature _____

~~CONFIDENTIAL~~
SECURITY INFORMATION

~~CONFIDENTIAL~~

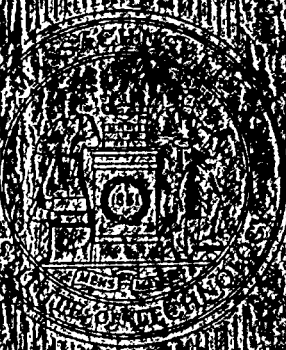
STUDY OF THE BEHAVIOR OF
CLOUDS OF CONTAMINANTS
IN THE LOWER ATMOSPHERE
OVER THE K-25 AREA

K-25 Site IRC
K-1002 MS 7221

GOVERNMENT
FINAL DETERMINATION
UNCLASSIFIED

AUTHOR

D. H. Egerton



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
RESEARCH SCHOOL

1962

Prepared under contract with the U.S. Atomic Energy Commission

under the terms of the contract between the U.S. Atomic Energy Commission

and the Massachusetts Institute of Technology

for the study of the behavior of clouds of contaminants

in the lower atmosphere over the K-25 area

RESTRICTED

K-1002, SO.

SECRET
SECURITY INFORMATION

~~SECRET~~
~~SECURITY INFORMATION~~

This document consists of 51 pages
Copy No. of 20 Series A.

Approved for Issue: T. H. Pigford

Report Number: K-904

Date of Issue: April 21, 1952

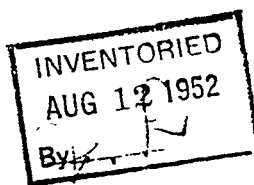
File Number: EPS-K134

Subject Category: SPECIAL

STUDY OF THE BEHAVIOR OF CLOUDS OF CONTAMINANTS
IN THE LOWER ATMOSPHERE OVER THE K-25 AREA

By

T. H. Pigford



X-RTV
X-REF.

~~RESTRICTED DATA~~

~~This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.~~

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Engineering Practice School

Prepared from work performed at the K-25 Plant of the
CARBIDE AND CARBON CHEMICALS DIVISION
Union Carbide and Carbon Corporation
Oak Ridge, Tennessee
Subcontract 70

CLASSIFIED BY CH-1152 6/30/57
By [signature]
7/26/57
E 904

~~SECURITY INFORMATION~~

This document has been approved for release
to the public by:

781 [signature] 7/26/96
Union Information Officer
Oak Ridge K-25 Site

~~SECURITY INFORMATION~~

2.

Report Number: K-904

Subject Category: SPECIAL

File Number: EPS-K134

Title: Study of the Behavior of Clouds
of Contaminants in the Lower
Atmosphere over the K-25 Area

Date of Issue: April 21, 1952

Author: T. H. Pigford

INTERNAL DISTRIBUTION

1. W. B. Humes
2. A. P. Huber
- 3-5. Engineering Division Central Files (Freida Dodge)
Attention: J. A. Connors
S. Cromer
F. R. McQuilkin
- 6-9. Safety and Protection Division Central Files (Margaret White)
Attention: H. F. Henry
K. P. Moseley
W. L. Richardson
S. L. Sullins
10. Plant Records, J. B. Sykes
K25RC
- 11-13. Plant Records, J. B. Sykes
- 14-18. M. I. T. Practice School (Joan Krupnick)

UNCLASSIFIED

~~SECRET~~

~~SECURITY INFORMATION~~

SECRET
SECURITY INFORMATION

Report Number: K-904

Subject Category: SPECIAL

File Number: EPS-K134

Title: Study of the Behavior of Clouds
of Contaminants in the Lower
Atmosphere over the K-25 Area

Date of Issue: April 21, 1952

Author: T. H. Pigford

EXTERNAL DISTRIBUTION

19. Engineering and Production Division, A. E. C., O. R. O.

20. U. S. Weather Bureau, A. E. C., O. R. O.
Attention: J. Z. Holland

UNCLASSIFIED
SECURITY INFORMATION

~~SECRET~~
~~SECURITY INFORMATION~~

4.

Report Number: K-904

Subject Category: SPECIAL

File Number: EPS-K134

Title: Study of the Behavior of Clouds
of Contaminants in the Lower
Atmosphere over the K-25 Area

Date of Issue: April 21, 1952

Author: T. H. Pigford

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Engineering Practice School

I. ABSTRACT

A study was made of the behavior of clouds of gases in the lower atmosphere over the K-25 Plant area, as simulated by smoke clouds released at various points in the area. "The evaporation rate of liquid hydrogen fluoride was measured under conditions simulating those of an accidental spill. The measured angles of spread of the smoke clouds are compared with the angles predicted from theory for those meteorological conditions which existed during these tests. From these data constants for the diffusion equations are evaluated, and distances for clouds resulting from an assumed spill of hydrogen fluoride to decrease in concentration to 122.3 ppm. are calculated." Recommendations are made for the safe storage of liquid hydrogen fluoride.

TABLE OF CONTENTS

	<u>Page</u>
I. ABSTRACT	4
II. SUMMARY	7
III. INTRODUCTION	9
IV. THEORETICAL CONSIDERATIONS	
A. Atmospheric Stability	10
B. Propagation of Clouds from Continuous Sources	11
C. Determination of Source of Strength Q	13
D. Propagation of Clouds formed Instantaneously	14
E. Quick Estimation of Angles of Spread and Determination of Effective Diffusion from Smoke Release	15
F. Effect of Buildings and Other Obstructions	16
V. PROCEDURE	
A. Meteorological Measurements	17
B. Release of Smoke Clouds	17
C. Determination of Atmospheric Evaporation Characteristics of Liquid Hydrogen Fluoride	19
D. Location of Original Data	20
VI. RESULTS AND DISCUSSIONS	
A. Summary of Meteorological Conditions Studied	21
B. Measured and Predicted Cloud Angles	21 7
C. Predicted Evaporation Rate and Distance for Persistence of Hydrogen Fluoride in Toxic Concentration from Continuous Release	31 2
D. Effect of Initial Flash of Superheated Liquid on Distance of Contamination	35 2

TABLE OF CONTENTS (continued)

	<u>Page</u>
E. Effect of Reaction of Dry Limestone on Contamination Distances	38
F. Practical Application of Results	39
VII. CONCLUSIONS	40
VIII. RECOMMENDATIONS	40
IX. APPENDIX	
A. Sample Calculations	41
B. Table of Nomenclature	50
C. Literature Citations	52
D. Acknowledgements	53

II. SUMMARY

This investigation was carried out to determine the behavior of clouds of gases released at various points in the K-25 Plant area and under various meteorological conditions, with particular emphasis on clouds of gaseous hydrogen fluoride. Such information would offer a basis for formulating safety and evacuation measures in the event of an accidental release of toxic gas.

Clouds of smoke were released from various locations, and aerial photographs were obtained as the clouds propagated over the plant area. Simultaneously, measurements of wind velocity and direction, atmospheric temperature gradient, and gustiness were obtained. In a separate experiment the evaporation rate of liquid hydrogen fluoride was measured under conditions simulating those of an accidental spill.

The measured angles of spread were compared with those computed with theory and based on the meteorological measurements, and this comparison is shown in Table I.

These data supply the necessary constants in the theoretical equations which predict the behavior of gas clouds in the lower atmosphere. From these equations the distances, measured from the point of release, required for a cloud of hydrogen fluoride to decrease in concentration to 122.3 ppm. were calculated for a possible spill of 5000 lb. of liquid hydrogen fluoride and for the following cases:

1. cloud resulting from the continuous evaporation of the spilled liquid,
2. cloud resulting from initial flash of the superheated liquid, and
3. cloud resulting from initial flash of the superheated liquid and from the reaction of hydrogen fluoride with dry calcium carbonate.

The calculated distances for various meteorological conditions are reported in Tables III and IV.

The following conclusions were reached:

1. Equations developed for the spread of clouds in the lower atmosphere over level terrain can be applied to the spread of toxic gases over the K-25 area if effective values of diffusion coefficients, as presented in Tables I and II, are used.

2. Due to the effect of local cross winds, building turbulence, and large variation in wind direction in this area, the observed angles of spread may be as much as five-fold greater than the predicted angles for lapse and as much as ninety-fold greater than the predicted angles for inversion.
3. For an assumed release of 5000 lb. of liquid hydrogen fluoride the distance required for the concentration of hydrogen fluoride to decrease to 122.3 ppm. may be on the order of 0.2 to 0.5 miles for lapse and 0.5 to 4 miles for inversion.
4. Unless the spill is extremely large and the liquid is allowed to spread freely over the ground, the main hazard is from flashing of superheated liquid hydrogen fluoride, rather than from continuous evaporation of unflashed liquid.
5. Storing liquid hydrogen fluoride over dry limestone increases the hazard from an accidental spill.

It is recommended that:

1. anhydrous liquid hydrogen fluoride be stored over an area surrounded by a dike so that spilled liquid will not spread freely over the area,
2. the storage vessel be surrounded by water sprays of large capacity and designed to go into action immediately in case of a spill, and
3. further studies be made of the rates of atmospheric evaporation of hydrogen fluoride under various meteorological conditions.

III. INTRODUCTION

The use and storage of large quantities of toxic gases in the K-25 area necessitate planning of adequate safety measures to insure against injury to plant personnel should an accidental release of these gases occur. The toxic gases handled in this area include hydrogen fluoride, ammonia, fluorine, chlorine, chlorine trifluoride, and uranium hexafluoride, which are stored and used at several locations in the plants. Due to the extreme toxicity of hydrogen fluoride, and because it is stored as a liquid in large quantities in a location, K-1132, upwind (based on the prevailing wind direction) of the plant area, the hazards resulting from the storage of this gas are of primary concern.

It was the purpose of this investigation to determine the behavior of clouds of gases released at various points in the plant area and under various meteorological conditions, with particular emphasis on clouds of gaseous hydrogen fluoride. Such information would offer a basis for formulating safety and evacuation measures in the event of an accidental release of toxic gas. Also, an evaluation was to be made of the means of storing large quantities of liquid hydrogen fluoride.

The behavior of clouds from a gas release can be predicted from theory (3, 10) only if the release is over a flat plain where there is no interference from buildings and terrain. The effect of buildings, of the size located at K-25, is to cause regions of recirculation of the gas cloud. In some cases buildings cause broadening of the area of contamination but shorten the distance the cloud travels before it is diluted to a tolerable concentration. Under other conditions the opposite effect, or some combination of these effects might be experienced. Because of these intangibles the theory cannot be trusted without experimental verification, and the most reasonable approach was to study the spread of gas clouds under conditions which would be encountered at K-25.

While it is not feasible to carry out such studies by releasing hydrogen fluoride in the plant area, previous work (10) has shown that hydrogen fluoride clouds should behave much the same as clouds of other gases or particulate matter, such as smoke. The approach which was to be followed was, therefore, to release smoke in various locations in the plant area and under various weather conditions, and to determine the cloud behavior from photographic measurements. Also, the rate of evaporation from spilled liquid hydrogen fluoride was to be studied in an area safely removed from the plant buildings.

In the following section the effect of meteorological conditions on propagation of clouds in the lower atmosphere is discussed, and theoretical equations which are used in predicting the behavior of such clouds are presented.

This investigation was carried out at the K-25 Plant from April 29, 1951, to July 5, 1951.

IV. THEORETICAL CONSIDERATIONS

A. ATMOSPHERIC STABILITY

Atmospheric pressure decreases with increasing altitude. If gas is expanded reversibly and adiabatically from a lower to a higher level, the temperature must decrease at a rate, as determined by the change in pressure with height, of about 1°C per 100 m., or 5.4°F per 1000 ft. for dry air (1). This is known as the adiabatic lapse rate. An atmosphere is stable, i.e., no vertical mixing due to buoyancy effects, when the rate of temperature decrease with height (defined as the lapse rate) is less than the adiabatic lapse rate.

Under lapse conditions the lapse rate is greater than the adiabatic lapse rate, and convective processes are set up which cause bulk motion from one layer to another. Lapse conditions usually occur during a sunny day, when solar radiation gives rise to temperature difference in the lower atmosphere.

On the other hand, during the night the earth loses heat, and the air layer near the ground becomes cooler than those layers at higher altitudes. Such conditions are known as inversion, and at low wind velocities are characterized by relatively little eddy mixing. Inversion may extend through the daylight hours if the sky is particularly overcast.

Lapse rates between zero and adiabatic in the lower atmosphere are usually referred to as neutral conditions.

Wind velocity also has a pronounced effect upon the stability of the lower atmosphere. Turbulence increases with increasing wind velocity, and at high wind velocities the temperature gradient during conditions for strong lapse or inversion may approach the adiabatic lapse rate due to increased heat transfer by eddy mixing.

In general, a cloud released in the lower atmosphere tends to dissipate rapidly during lapse but persists much longer during inversion. Increasing wind velocity tends to increase the rate of dissipation.

Because the transfer and dissipation of dispersed material in the atmosphere is largely by eddy diffusion rather than by molecular diffusion, the nature of the chemical species is of little importance, and the diffusion equations which will be presented apply equally well to gases and particulate matter such as smoke. It is recognized that some differences may occur during conditions of high humidity or rainfall if one material is very soluble in water, but such characteristics will be ignored in the quantitative treatment of the data obtained in this work. It is assumed throughout that any characteristics of cloud behavior observed for smoke clouds will be the same for clouds of other material.

B. PROPAGATION OF CLOUDS FROM CONTINUOUS SOURCES

For the behavior of a cloud of material, such as smoke or gas, released over a flat terrain and from a continuous point source at ground level Sutton (10) has developed the equation:

$$\chi = \frac{2Q}{\pi C_y C_z \bar{u} x^{2-n}} \exp \left[-\frac{1}{x^{2-n}} \left(\frac{y^2}{C_y^2} + \frac{z^2}{C_z^2} \right) \right] \quad (1)$$

where:

x, y, z = distances in meters from the point source downwind, crosswind, and vertical

χ = concentration at any point x, y, z , in g./cu. m.

\bar{u} = mean wind velocity in m./sec.

Q = source strength in g./sec.

C_y, C_z = diffusion coefficients in the crosswind and vertical directions, (m.)ⁿ

The exponent n is known as the atmospheric stability term, and is defined by the velocity-profile relation:

$$\frac{\bar{u}_2}{\bar{u}_1} = \left(\frac{z_2}{z_1} \right)^{\frac{n}{2-n}} \quad (2)$$

Values of n may vary from zero to unity, with low values characterizing lapse conditions and values nearer unity characterizing inversion.

Rather than measure wind velocity at various heights to determine n , it is easier to measure the temperature gradient. Holland (5) has developed a graph which correlates empirically the stability term n as a function of temperature gradient. This correlation is based on a large number of simultaneous measurements of velocity and wind profiles in the Oak Ridge area. Values of n used in the present study were derived from temperature-gradient observations by means of Holland's graphical correlation.

The diffusion coefficients are defined by:

$$C_y^2 = \frac{4\mathcal{V}^n}{(1-n)(2-n)\bar{u}^n} \left(\frac{\overline{v'^2}}{\overline{u^2}} \right)^{1-n} \quad (3)$$

$$C_z^2 = \frac{4\mathcal{V}^n}{(1-n)(2-n)\bar{u}^n} \left(\frac{\overline{w'^2}}{\overline{u^2}} \right)^{1-n} \quad (4)$$

where:

v', w' = crosswind and vertical eddy velocities in m./sec.

\mathcal{V} = kinematic viscosity of air in sq. m./sec.

The terms $\overline{v'^2}/\overline{u^2}$ and $\overline{w'^2}/\overline{u^2}$ are measures of the intensity of turbulence, or "gustiness", in the y and z direction.

Equations (3) and (4) are approximated by Holland (8) as:

$$C_z^2 = C_y^2 = \frac{4\mathcal{V}^n}{(1-n)(2-n)\bar{u}^n} (\tan \sigma_\theta)^{2-2n} \quad (5)$$

where σ_θ is the standard deviation of the instantaneous angular deviation θ of the wind from the mean direction, and is determined statistically from a recording of instantaneous wind directions as measured by a sensitive wind vane.

Thus, from measurements of gustiness, temperature gradient, and mean wind velocity, and for a source of given strength, the concentration of diffusing material may be predicted from equation (1).

To obtain concentrations at ground level and directly downwind from the source (y and z equal zero), equation (1) becomes

$$\chi = \frac{2Q}{\pi C_y C_z \bar{u} x^{2-n}} \quad (6)$$

or, solving for x:

$$x = \left[\frac{2Q}{\pi C_y C_z \bar{u} \chi} \right]^{\frac{1}{2-n}} \quad (7)$$

However, equations (1) and (7) predict an infinite concentration at the point of release, which is not realistic. If the concentration directly above the point of release is some infinite value χ_0 , the fictitious distance x_0 from the actual point of release upwind to a virtual point source of infinite concentration may be calculated from equation (1). The actual distance downstream x_c for the downwind, ground-level concentration to decrease to χ_t is then:

$$x_c = \left[\frac{2Q}{\pi C_y C_z u} \right]^{\frac{1}{2-n}} \left[\left(\frac{1}{\chi_t} \right)^{\frac{1}{2-n}} - \left(\frac{1}{\chi_0} \right)^{\frac{1}{2-n}} \right] \quad (8)$$

C. DETERMINATION OF SOURCE STRENGTH Q

For the spill of a volatile liquid, such as hydrogen fluoride, a portion of the liquid may flash and the remainder will flow along the ground or collect in pools. The unflashed liquid will soon reach a steady-state temperature and from then on will gradually vaporize as sufficient heat is received by transfer from the air or from the ground. If it is assumed that transfer of heat from the air is controlling, the rate of evaporation Q may be related to wind velocity and stability by Calder's approximation (3):

$$Q = P_V \left(a + b u^{\frac{2-n}{2+n}} \right) \quad (9)$$

where:

P_V = vapor pressure of evaporating liquid, lb./sq. in. (absolute)

a, b = constants

From experiments on the evaporation of hydrogen fluoride into the atmosphere under various meteorological conditions the constants in equation (9) may be evaluated for this liquid.

With this information, equations (8) and (9) may be used to predict the behavior of clouds resulting from the continuous evaporation of spilled hydrogen fluoride and under various weather conditions.

D. PROPAGATION OF CLOUDS FORMED INSTANTANEOUSLY

The propagation of a cloud formed almost instantaneously from flashed vapor at the time of the spill may be approximated by Calder's equation (3):

$$\chi = \frac{2W}{\pi^{3/2} C_x C_y C_z (\bar{u}t)^{3(2-n)/2}} \exp \left[\frac{-r^2}{(C_x C_y C_z)^{2/3} (\bar{u}t)^{2-n}} \right] \quad (10)$$

where:

- W = amount of dissipating material in the cloud, g.
- r = distance from the center of the cloud to the point where χ is measured, m.
- t = time elapsed since the initial formation of the cloud, sec.

For the purposes of this investigation the limit of cloud propagation is taken as that distance x_f measured from the point of release, at which the concentration at the center of the cloud is equal to the limiting concentration χ_t . In this case r is zero and $x = \bar{u}t$. As in the development of equation (8), it is necessary to correct for the fictitious distance x_0 for the concentration to reach the finite value χ_0 at the point of release. Equation (10) then becomes:

$$x_f = \left[\frac{2W}{\pi^{3/2} C_x C_y C_z} \right]^{2/3(2-n)} \left[\left(\frac{1}{\chi_t} \right)^{2/3(2-n)} - \left(\frac{1}{\chi_0} \right)^{2/3(2-n)} \right] \quad (11)$$

For an assumed amount of spill, the weight flashed W may be calculated knowing the conditions under which the liquid was stored. Other terms are determined as before.

E. QUICK ESTIMATION OF ANGLES OF SPREAD AND DETERMINATION OF
EFFECTIVE DIFFUSION COEFFICIENTS FROM SMOKE RELEASE

If equation (1) is solved for the point y_0 at ground level at which the concentration of the diffusing material is one-tenth, the corresponding ground-level concentration directly downstream of the source (where y and z are zero), the following results:

$$y_0 = (\ln 10)^{1/2} C_y (x)^{1 - \frac{n}{2}} \quad (12)$$

The coordinates (x, y_0) are useful in defining the boundaries of a cloud propagating from a point source. Although the definition of y_0 is purely arbitrary, and even though the cloud boundary defined by (x, y_0) is not a boundary of constant concentration, these limitations are not too important since it can be shown that at points not far removed from the source the cloud boundaries defined by a wide range of concentrations are very nearly the same (5). Throughout this work it will be assumed that the cloud boundary near the point of release, as estimated from photographs of smoke release, is essentially the same as that defined by equation (2).

The mean angle of cloud spread α may be defined as:

$$\alpha = 2 \tan^{-1} (y_0/x) \quad (13)$$

Although y_0/x decreases slightly as x increases, this is a good approximation when not far from the point of release. Since clouds studied here are in every case still persistent at a distance 100 meters from the source, a value of x of 100 meters is used as the reference point at which cloud angles are measured.

Combining equations (12) and (13), and using 100 meters for x ,

$$\alpha = 2 \tan^{-1} \frac{1.52 C_y}{10^n} \quad (14)$$

Thus, if the stability term n and the lateral diffusion coefficient C_y are determined from meteorological observations as described in a previous section, angles of cloud spread in the vicinity of the release may be quickly calculated from equation (14).

Conversely, from a photograph taken looking downward on a smoke cloud, values of the effective lateral diffusion coefficient C_y may be calculated from equation (14), using as α the angle subtended by the visible boundaries of the cloud at 100 meters from the source.

A more precise estimate of the ground-level cloud boundaries, when the boundaries are defined by some tolerance concentration χ_t , is determined by solving equation (1) for x and y , with z equal to zero:

$$y_c = C_y(x)^{1 - \frac{n}{2}} \left[- \ln \frac{\pi C_y C_z \bar{u}(x)^{2-n} \chi_t}{2Q} \right]^{1/2} \quad (15)$$

In this case the correction for a virtual point source upstream, as mentioned in the discussion prior to equation (8), is neglected.

F. EFFECT OF BUILDINGS AND OTHER OBSTRUCTIONS

It should be emphasized that equations (1) and (10) have been derived, and experimentally verified, for the case of a cloud propagating over a flat terrain and are not expected to apply quantitatively when large buildings and other obstructions are interposed in the cloud path. In the latter case, the building would introduce additional turbulence and would cause the cloud to dissipate more rapidly. Also, local cross flow may be induced in the spaces, streets, and alley-ways between buildings which would cause the cloud to propagate locally in a direction other than the mean wind direction.

In spite of these limitations, these equations serve as reasonable and useful methods for predicting the behavior of clouds under various meteorological conditions. Comparisons between the cloud behavior predicted from these idealized equations and that observed from smoke-cloud experiments are made in a following section.

V. PROCEDURE

The experimental procedure consisted of three main phases: (1) measurement of meteorological conditions, (2) release of smoke clouds at various locations in the plant areas, and (3) determination of the atmospheric evaporation characteristics of liquid hydrogen fluoride. Phases (1) and (2) were carried out simultaneously.

For the purpose of orientation, a simplified map of the plant area is shown in Figure 1.

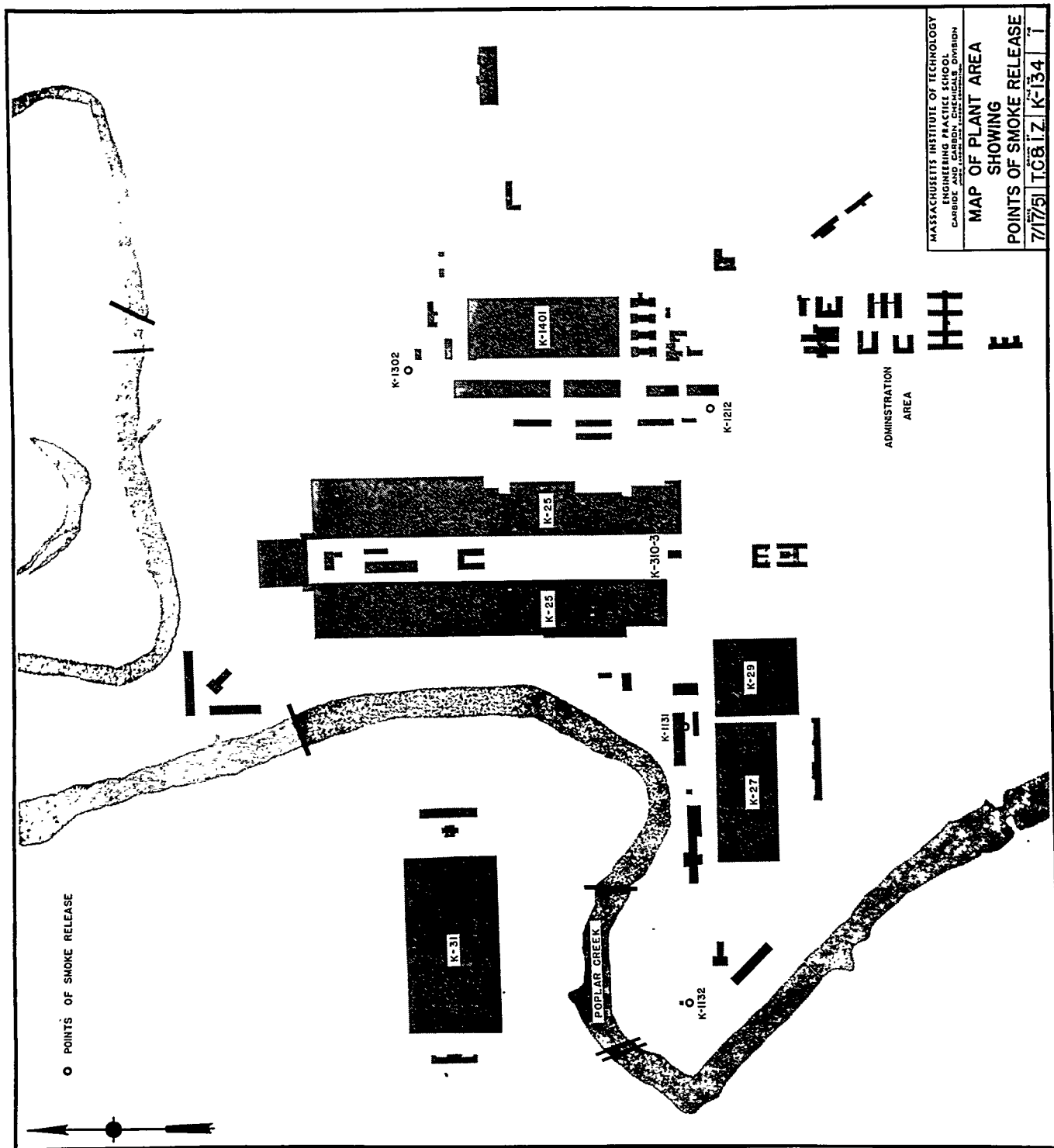
A. METEOROLOGICAL MEASUREMENTS

1. Wind velocity \bar{u} was measured at two locations, K-302-4 and K-1132, with cup-type anemometers.
2. Thermopiles were installed at heights of 5 and 55 ft. on a guard tower, K-1017-S-18, near K-1132, to measure the temperature gradients. These thermopiles became inoperative during the week of these experiments, and temperature gradients were finally obtained from resistance thermometers which had been installed on the X-10 water tower by the O.R.N.L. Health Physics group.
3. Gustiness measurements, σ_{θ} , were obtained from the recordings of the time variation in wind direction, as indicated by sensitive wind-direction indicators (7) which had been installed above buildings K-832 and K-302-4 by the U. S. Weather Bureau group.

B. RELEASE OF SMOKE CLOUDS

The smoke pots used to form smoke clouds were obtained from the U. S. Weather Bureau group at Oak Ridge. These were the HC-Type U. S. Army Smoke Pots which released zinc-chloride smoke resulting from the combustion of zinc chloride and hexachloroethane. Each smoke pot burned from 6 to 10 min. and released about 10 lb. of white-grey smoke. The smoke pots were fired singly, in series, or simultaneously, depending upon the requirements for the formation of a visible cloud of satisfactory coverage.

In order to obtain a satisfactory perspective of smoke clouds released simultaneously from several locations, it was necessary to obtain aerial photographs of the clouds. A two-place Air Force helicopter and a photographic crew were obtained from Wright Field through arrangements made by



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
 ENGINEERING PRACTICE SCHOOL
 CARBIDE AND CARBON CHEMICALS DIVISION

MAP OF PLANT AREA
 SHOWING
 POINTS OF SMOKE RELEASE

7/17/51 TC81Z K-134 1

the Atomic Energy Commission. The photographs were taken when the helicopter was flying over the outer boundaries of the K-25 area and at an altitude of approximately 3000 ft.

Photographs of the smoke clouds were also obtained by photographers stationed on top of K-31 and K-27.

During each run sufficient photographs were obtained to indicate the behavior of each smoke cloud as it progressed over the plant area.

Eleven runs were made over a four-day period, so that the smoke-cloud photographs and meteorological measurements were obtained under a variety of meteorological conditions.

During these tests smoke was released from K-1132, from the top of K-310-3 and from ground level near K-1132, K-1302, and K-1212. Smoke was also released through the stack at K-1131, and these latter data were turned over to the K-25 Design and Development Department for analysis.

C. DETERMINATION OF ATMOSPHERIC EVAPORATION

CHARACTERISTICS OF LIQUID HYDROGEN FLUORIDE

An evaporation pan 2.29 x 3.79 ft. on the sides and 5/8 in. deep was placed in a level position in an open field removed from the immediate plant area. At the beginning of the test the pan was filled from a 230-lb. cylinder of anhydrous liquid hydrogen fluoride. The data obtained follow:

1. time for level of hydrogen fluoride in the pan to decrease to a predetermined level,
2. temperature of the liquid hydrogen fluoride in the pan, as measured by a nickel-sheathed thermocouple, and
3. wind velocity, as measured by a vane-type anemometer.

The vertical temperature gradient which was assumed to be characteristic of the meteorological conditions during these evaporation tests was later obtained from the records of the U. S. Weather Bureau at Oak Ridge.

After the initial flash due to superheat of the liquid from the hydrogen-fluoride cylinder, the evaporation rate appeared to be fairly constant, and the liquid temperature was essentially constant at about -8°C.

One run was made to determine the effect of dry calcium carbonate in the evaporation pan when the liquid hydrogen fluoride was added. Although no quantitative data were obtained, the rate of evolution of hydrogen fluoride gas was observed to be much greater than in the previous test, where no calcium carbonate was present.

D. LOCATION OF ORIGINAL DATA

The original data of this investigation are located in Notebook No. 1801, assigned to the M.I.T. Engineering Practice School at the K-25 Plant. Photographs obtained in this work are on file at K-25 Plant Records Department.

VI. RESULTS AND DISCUSSION

A. SUMMARY OF METEOROLOGICAL CONDITIONS STUDIED

The meteorological conditions which existed when the behavior of smoke clouds was studied are listed in Table I. It is evident that these tests covered a wide range of conditions from lapse to inversion. Typical photographs of the smoke clouds are shown in Figures 2 through 6.

B. MEASURED AND PREDICTED CLOUD ANGLES

Values of the angle of spread α , as measured from the point of release to the visible boundaries of the cloud (when looking down from above) at a distance of 100 m. from the source, are listed in Table II. Also listed are the angles predicted from the meteorological measurements and effective values of the lateral diffusion coefficient C_y calculated from the measured angles (cf. equation (14) and Sample Calculations).

It is evident that the best agreement between observed and predicted angles occurs during lapse at the highest wind velocity (cf. Run 3). The agreement during the other lapse runs (cf. Runs 1, 2, 3, 5, 6, and 9) is generally good, although the predicted angles for these runs vary from 1.2 times the observed angle (Run 2, K-1132) to less than one-fifth the observed angle (Run 9, K-310-3). The poor agreement in the latter case may be due to the existence of local cross winds in the area, as evidenced by the extremely large value of σ_θ measured at K-832 during the same run.

The poorest agreement between observed and predicted angles occurs during inversion (Runs 4, 7, 8, 10, and 11) where the observed angles are from approximately three-fold (Run 10, K-310-3) to sixty-fold (Run 7, K-310-3) greater than the predicted values. Since inversion holds a cloud near the ground and forces it to flow near and around buildings, turbulence and local cross flow should be less important during lapse than during inversion. Also, any extraneous disturbances can have a relatively large effect upon cloud spread during inversion, since the normal level of atmospheric turbulence is low during this period.

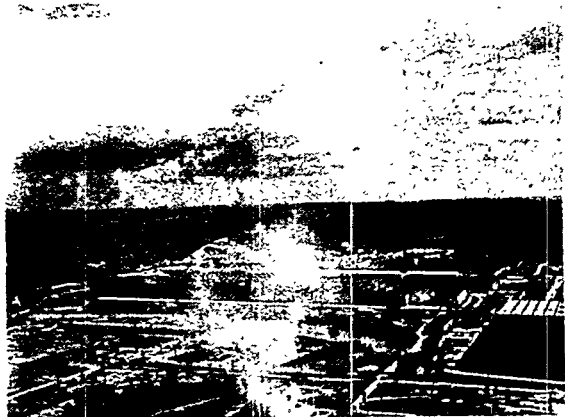
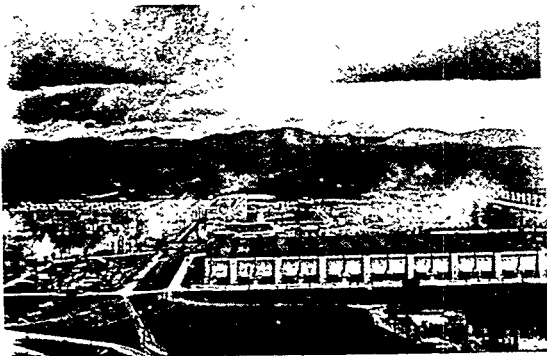
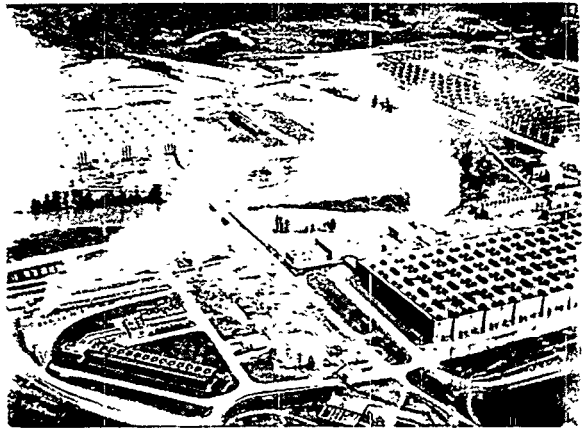
In every test carried out during inversion conditions the wind velocity was quite low--never greater than 5 miles/hr. Since a cloud propagates and dissipates more slowly at low wind velocities, the cloud would be spread over a large angle from the source due to the slow--but significant--changes in wind direction which occurred throughout each of these tests.

TABLE I
SUMMARY OF EXPERIMENTAL RUNS AND METEOROLOGICAL CONDITIONS

Run	Date	Time	(1) Lapse Rate °F 100 ft.	Conditions	n	Measurements at K-302-4			Measurements at K-832		
						Wind Velocity	σ_θ	C_y	Wind Velocity	σ_θ	C_y
						miles/hr.	degrees	(m.) ⁿ	miles/hr.	degrees	(m.) ⁿ
1	6/12	15:30	- 1.1	lapse	0.26	4	18	0.16	4	48	0.33
2	6/13	11:50	- 2.2	lapse	0.20	9	23	0.24	9	44	0.47
3	6/13	14:30	- 2.2	lapse	0.20	13	18	0.20	12	33	0.34
4	6/13	19:30	+ 0.6	inversion	0.46	4	20	0.087	3	26	0.11
5	6/14	10:30	- 1.7	lapse	0.22	4	45	0.47	4	34	0.35
6	6/14	13:30	- 1.7	lapse	0.22	9	32	0.30	8	48	0.50
7	6/15	06:00	+ 1.7	inversion	0.63	5	18	0.047	1	30	0.089
8	6/15	08:30	0	inversion	0.38	3	24	0.13	2	7	0.062
9	6/15	14:30	-1.7	lapse	0.22	6	25	0.25	4	60 ⁽²⁾	0.71
10	6/15	17:30	0	inversion	0.38	5	16	0.094	5	30	0.15
11	6/15	19:30	+ 1.7	inversion	0.63	3	13	0.046	1	37	0.10

Notes: (1) Measured by thermocouples at 183 ft. and 4 ft. above ground level. at X-10. A negative value indicates temperature decreasing with height.

(2) Deviations exceeded maximum range of instrument. σ_θ was assumed to equal 60°.



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

LAPSE

SMOKE RELEASED FROM K-II32

RUN 2

6-13-51

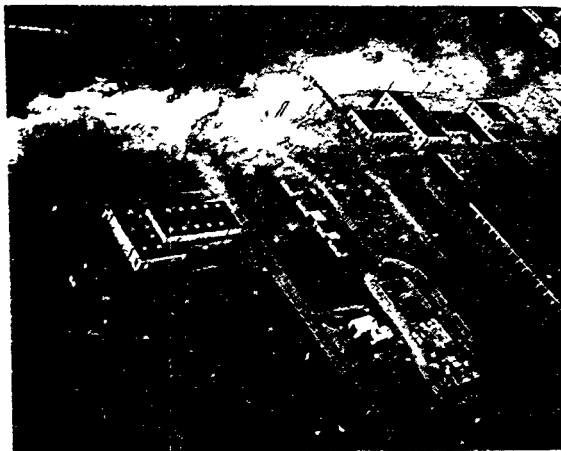
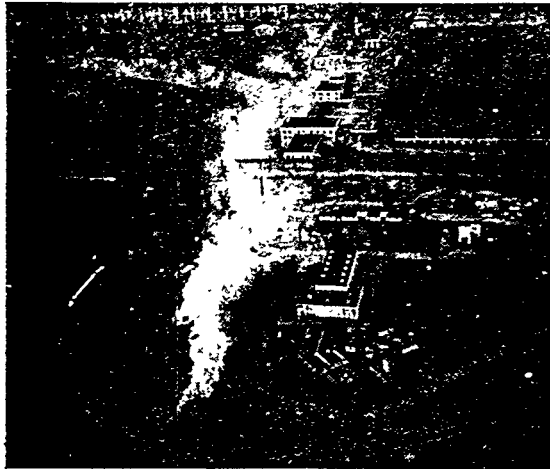
11:50

DATE
3-8-52

DRAWN BY
W.L.M

FILE NO.
EPS K-134

FIG.
2



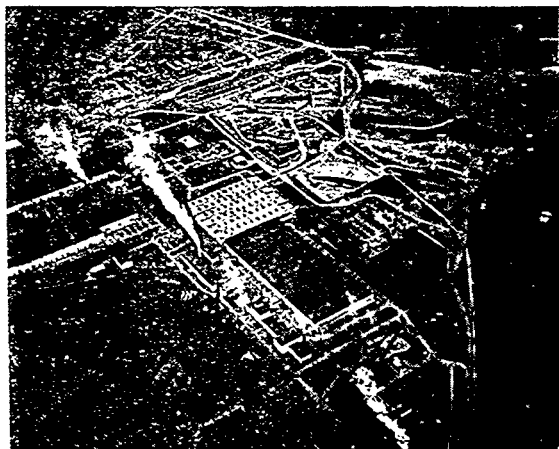
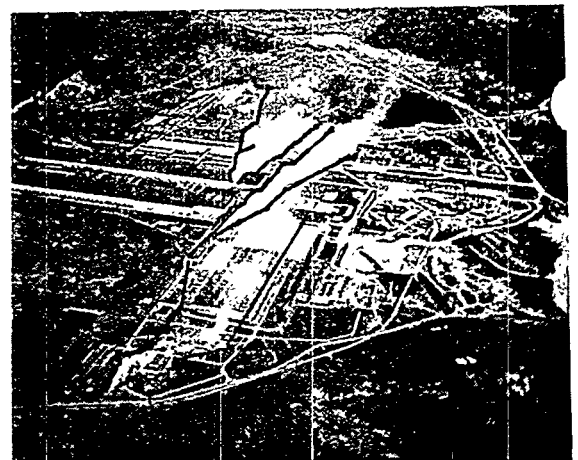
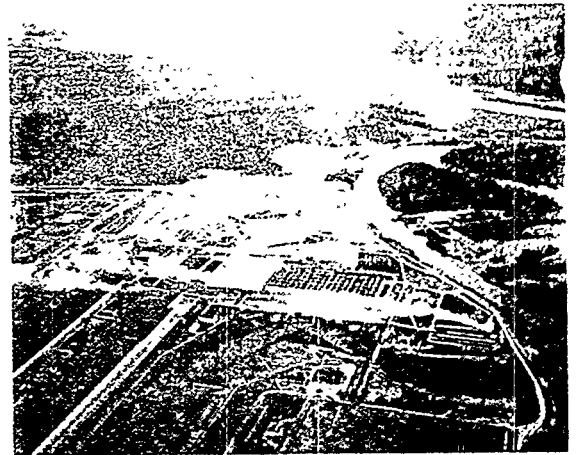
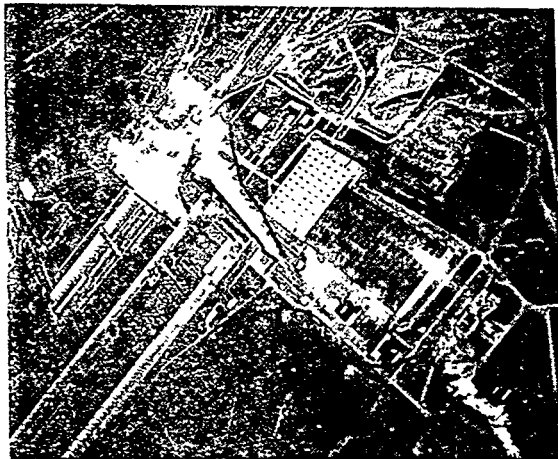
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

INVERSION

SMOKE RELEASED FROM K-1132

RUN 4 6-13-51 19:30

DATE	DRAWN BY	FILE NO.	FIG.
3-8-52	W.L.M.	EPS K-134	3



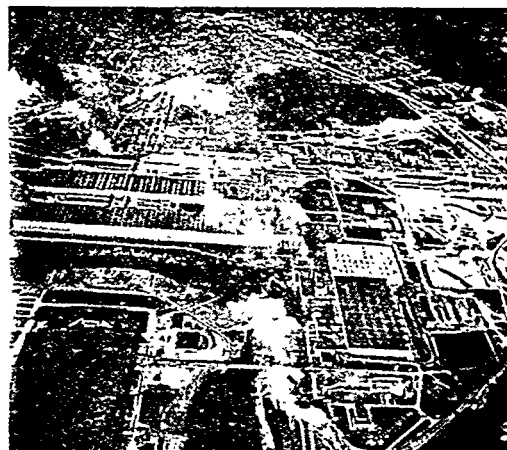
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

INVERSION

SMOKE RELEASED FROM K-II32
K-II31 AND K-310-3

RUN 4 6-13-51 19:30

DATE 3-8-52	DRAWN BY W.L.M.	FILE NO. EPS K-134	FIG. 4
----------------	--------------------	-----------------------	-----------



SMOKE RELEASED FROM K-1132

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

INVERSION

SMOKE RELEASED FROM K-1132

K-1131, K-1212, and K-1302

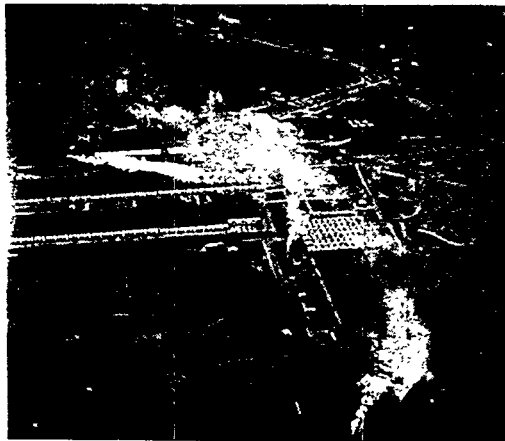
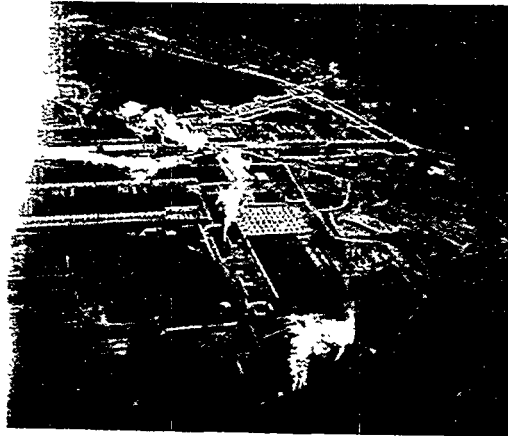
RUN 10 6-15-51 1730

DATE
3-8-52

DRAWN BY
W.L.M.

FILE NO.
EPS K-134

FIG.
5



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

INVERSION, LOW WIND VELOCITY
SMOKE RELEASED FROM K-1132
K-1131 and K-1302

RUN II 6-15-51 1930

DATE
3-8-52

DRAWN BY
W.L.M.

FILE NO.
EPS K-134

FIG.
6

TABLE II

MEASURED AND PREDICTED CLOUD ANGLES, AND DIFFUSION COEFFICIENTSCALCULATED FROM MEASURED CLOUD ANGLES

Run	Measured Angles, degrees			Predicted Angles, degrees		Lateral Diffusion Coefficient, C _y , Calculated from Measured Cloud Angle	
	Source at K-1132	Source at K-310-3	Source at K-1202	Source at K-1302	Based on Measurements at K-302-4	Based on Measurements at K-832	
					(near K-310-3)	(near K-1132)	(m.) ⁿ
1	44	31	--	--	21	30	0.48
2	39	39	--	40	31	47	0.37
3	44	39	--	40	26	35	0.42
4	37	35	--	--	5	7	0.64
5	68	91	67	86	52	34	0.74
6	60	68	--	39	32	47	0.63
7	185	114	68	34	2	4	--
8	23	70	51	48	10	4	0.32
9	119	170	89	99	32	68	1.86
10	37	30	90	90	9	10	0.53
11	83	--	65	18	2	4	2.48

The cloud would then persist for a long period of time at a high concentration in the vicinity of the source and would be evident in photographs. This is probably the most important factor which contributes to the large discrepancies between predicted and observed angles. During one test the wind direction was found to change by as much as 180° over a period of approximately 10 minutes.

Values of the lateral diffusion coefficient C_y which have been calculated from the measured angles may be considered the effective values which take into account the additional cloud-dissipating mechanisms described above. These values may be used to estimate cloud behavior in this immediate area under similar conditions of lapse rate, wind velocity, and gustiness.

C. PREDICTED EVAPORATION RATE AND DISTANCE FOR
PERSISTENCE OF HYDROGEN FLUORIDE IN TOXIC
CONCENTRATION FROM A CONTINUOUS RELEASE

Insufficient data were obtained for the evaporation of hydrogen fluoride to evaluate the values of both constants in the evaporation equation (9). It was assumed that a was small relative to

$$b(\bar{u})^{\frac{2-n}{2+n}},$$

and the evaporation rate was approximated as:

$$Q = A m (\bar{u})^{\frac{2-n}{2+n}} \quad (16)$$

where:

A = area of evaporating surface, sq. m.

m = $3.68 \text{ g./}(\text{sec.})(\text{sq. m.})(\text{m./sec.})^{\frac{2-n}{2+n}}$

In applying this equation to the atmospheric evaporation of hydrogen fluoride resulting from an accidental spill, it is assumed that:

1. After the initial flash or superheated liquid resulting from a spill, the surface temperature of the evaporating liquid remains constant at about -8°C, which was the temperature observed in the evaporation experiments. This temperature would actually vary somewhat with varying rates of heat transfer from the air to the liquid, from the ground to the liquid, and from the bulk liquid to the surface layer.

2. The spilled liquid does not react with any neutralizing agent such as limestone, and is not diluted with water. In the latter case the value of m would be considerably decreased, as the evaporation rate is proportional to the equilibrium partial pressure of hydrogen fluoride over the evaporating solution.

The surface area for evaporation A can be written in terms of the amount spilled, as:

$$A = \frac{(1 - k)M}{\rho_L h} \quad (17)$$

where:

$$k = \frac{H_{L1} - H_{L2}}{\Delta H_V - H_{L2}}$$

H_{L1} = enthalpy of liquid HF at storage conditions, B.t.u./lb.

H_{L2} = enthalpy of saturated liquid HF at atmospheric pressure, B.t.u./lb.

ΔH_V = enthalpy of vaporization from saturated HF at atmospheric pressure, B.t.u./lb.

M = total amount spilled, g.

ρ_L = density of spilled liquid, g./cu. m.

h = depth of pool of spilled liquid, m.

The contamination distance x_c required for the cloud resulting from continuous evaporation to decrease in concentration to χ_t is obtained by combining equations (8), (16), and (17):

$$x_c = \left[\frac{2m(1 - k)M}{\tilde{n} \rho_L h C_y C_z (\bar{u})^{\frac{2n}{2-n}}} \right]^{\frac{1}{2-n}} \left[\left(\frac{1}{\chi_t} \right)^{\frac{1}{2-n}} - \left(\frac{1}{\chi_o} \right)^{\frac{1}{2-n}} \right] \quad (18)$$

To illustrate the order of magnitude of the contamination distances which would be expected to result from a spill of liquid hydrogen fluoride the following conditions are assumed:

1. A spill of 5000 lb. of anhydrous liquid hydrogen fluoride occurs.

2. The unflashed liquid spreads on the ground to form a pool 1 in. deep.
3. The contamination distance x_c extends to that point where the concentration χ_t is 122.3 ppm., which is the concentration of hydrogen fluoride in air that is injurious to personnel upon short exposure (2).
4. The ambient temperature is 75°F.
5. The liquid hydrogen fluoride is stored at 85°F (higher than ambient temperature due to solar radiation).

For these assumed conditions the surface area for evaporation is calculated to be 890 sq. ft. Substituting proper constants, equation (18) becomes:

$$x_c = \left[\frac{1933}{C_y C_z} \right]^{\frac{1}{2-n}} \left(\frac{1}{\pi} \right)^{\frac{2n}{4-n^2}} \quad (18a)$$

From the data obtained in this work there are two rational bases for choosing values of diffusion coefficients:

1. Isotropic turbulence for the cloud as a whole is assumed. The values of C_x and C_z are assumed to be equal to those values of C_y predicted from meteorological measurements.
2. Anisotropic turbulence is assumed. It is possible that in that region immediately above the buildings where the gustiness factor σ_0 was measured, isotropic turbulence occurs locally. The vertical diffusion coefficient C_z then equals the local value of C_y obtained from meteorological measurements. The effective value of C_y for the cloud as a whole is then assumed to be that determined from the observed angle of cloud spread (cf. Table II).

Required distances calculated on both bases are presented in Table III.

Since the effective values for the lateral diffusion coefficient C_y are generally larger than those predicted from meteorological measurements (as discussed in the previous section), the predicted distances assuming anisotropic turbulence are generally less than those for which isotropic turbulence has been assumed.

The distances predicted for inversion are generally greater than those predicted for lapse, as would be expected.

TABLE III
EVAPORATION RATES AND CONTAMINATION DISTANCES FOR
CONTINUOUS RELEASE OF HF

Predicted Distance for HF Concentration to Decrease to 122.3 ppm. ⁽¹⁾ miles						
<u>Run</u>	<u>Predicted Evap- oration Rate⁽²⁾ lb./min.</u>		<u>K-302-4 and K-310-3</u>		<u>K-832 and K-1132</u>	
	<u>K-302-4</u>	<u>K-832</u>	<u>For Isotropic Turbulence</u>	<u>For Anisotropic Turbulence</u>	<u>For Isotropic Turbulence</u>	<u>For Anisotropic Turbulence</u>
1	63	63	0.34	0.24	0.15	0.12
2	120	120	0.19	0.14	0.082	0.094
3	170	160	0.21	0.15	0.11	0.10
4	58	49	1.7	0.50	1.5	0.44
5	65	65	0.14	0.058	0.13	0.085
6	120	115	1.4	0.084	0.080	0.071
7	61	27	1.8	0.68	7.0	—
8	50	40	0.77	0.20	2.0	0.74
9	89	65	0.18	—	0.059	0.034
10	68	68	1.0	0.44	0.58	0.26
11	47	27	21.7	—	6.0	0.56

Notes: (1) For the cloud resulting from continuous evaporation only.
 (2) Steady-state evaporation rate after initial flash for an assumed spill of 5000 lb. and a liquid depth of 1 in.

Although there are considerable variations in predicted distances, those distances calculated on the basis of anisotropic turbulence should be of the same order of magnitude as the actual distance of contamination which would result under these conditions.

The choice of a 5000 lb. spill and a liquid depth of 1 in. was entirely arbitrary. If a greater amount of liquid were spilled, or if the liquid were allowed to spread in an even thinner pool, the contamination distance would increase, and contamination distances for other conditions may be predicted from equation (18).

Clearly, one method of reducing the contamination distance is to provide some means of reducing the surface area of the spilled liquid. This could be accomplished by erecting a dike around the area immediately below the hydrogen-fluoride storage tanks to prevent the spilled liquid from spreading over a large area. With such precaution the contamination distance would be essentially independent of the amount spilled, since the surface area for evaporation would remain constant. The time required for the spilled liquid to be dissipated would increase proportionally with the amount spilled.

It is important to note that the above considerations ignore the effect of flashing of the superheated liquid at the time of the spill. This, and an evaluation of methods of neutralizing or diluting the spilled hydrogen fluoride are discussed in following sections.

D. EFFECT OF INITIAL FLASH OF SUPERHEATED LIQUID ON DISTANCE OF CONTAMINATION

If the temperature at which liquid hydrogen fluoride is stored is greater than 67°F, the temperature at which the vapor pressure of anhydrous fluoride is 1 atm., a portion of the liquid will flash into vapor when a spill occurs. This flash would form a cloud almost instantaneously, and the distance of travel of the cloud before the concentration of hydrogen fluoride in the center of the cloud decreases to the toxic concentration can be predicted from equation (11).

The effect of flashing can be illustrated by calculating the contamination distances on the basis of the assumed spill described in the previous section. It is also assumed that the liquid flashes instantaneously and that the center of the resulting cloud consists of pure hydrogen fluoride at the ambient temperature.

It is assumed that isotropic turbulence occurs only in the horizontal plane, so that C_x and C_y have values determined from the observed angle

of cloud spread. Values of C_z are assumed equal to the values of C_z determined from meteorological readings.

The resulting contamination distances are presented in Table IV. These distances may be compared with those predicted for a continuous evaporation and for anisotropic turbulence (cf. Table III). It is evident that the potential hazard due to the initial flash is generally greater than that resulting from continuous evaporation, although the converse is true when the effective horizontal diffusion coefficients are very large (cf. Runs 8 and 11, K-832 and K-1132). The hazard due to flash increases as the temperature of the stored liquid increases.

The relative importance of flash as opposed to continuous evaporation is further illustrated by the following equation, which neglects the upstream virtual point source:

$$\frac{x_f}{x_c} = \left\{ \frac{C_y C_z \chi_t}{2M} \left(\frac{k}{C_x} \right)^2 \left[\frac{\rho_L h}{m(1-k)} \right]^3 \right\}^{\frac{1}{3(2-n)}} \cdot (\bar{u})^{\frac{2n}{4-n^2}} \quad (19a)$$

Thus, if the depth of spilled liquid h is assumed constant, the relative importance of flash increases as wind velocity increases and as the amount spilled M decreases.

If the surface area of spilled liquid is held constant by a dike or some such means, equation (19a) can be rewritten as

$$\frac{x_f}{x_c} = \left[\frac{C_y C_z \chi_t}{2(Am)^3} \left(\frac{kM}{C_x} \right)^2 \right] (\bar{u})^{\frac{2n}{4-n^2}} \quad (19b)$$

In this case the relative importance of flash increases with increasing amount spilled M .

An effective method of decreasing the hazard due to flash would be to provide water sprays about the storage vessel, with the sprays designed to go into action automatically in case of a spill. Although there is a considerable heat of solution of hydrogen fluoride in water, this could be absorbed by a sufficient excess of water. Because of high solubility of gaseous hydrogen fluoride in water the sprays should absorb significant portion of the flash cloud that is formed.

The dilution of unflashed liquid with excess water should be effective in decreasing the rate of continuous evaporation, thereby decreasing the contamination distance due to this effect.

TABLE IV

CONTAMINATION DISTANCES FOR CLOUD RESULTING FROM FLASH
OF LIQUID HYDROGEN FLUORIDE AND CHEMICAL REACTION⁽¹⁾

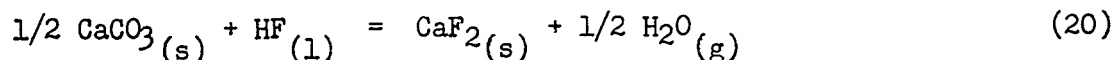
Run	For K-302-4 and K-310-3				For K-832 and K-1132					
	Diffusion		Contamination		Diffusion		Contamination			
	Coefficients Used		Distance		Coefficients Used		Distances			
	(m.) ⁿ		miles		(m.) ⁿ		miles			
	C_x, C_y	C_z (2)	C_z (3)	x_f Flash Only	x_{f+r} Flash Plus Chemical Reaction	C_x, C_y	C_z (2)	C_z (3)	x_f Flash Only	x_{f+r} Flash Plus Chemical Reaction
1	0.33		0.16	0.43	0.70	0.48		0.33	0.24	0.40
2	0.37		0.24	0.26	0.42	0.37		0.47	0.22	0.36
3	0.37		0.20	0.30	0.49	0.42		0.34	0.22	0.36
4	0.60		0.087	0.58	1.0	0.64		0.11	0.50	0.88
5	1.12		0.47	0.10	0.16	0.74		0.35	0.16	0.26
6	0.74		0.30	0.16	0.26	0.63		0.50	0.15	0.24
7	0.43		0.047	3.6	6.8	---		0.089	---	---
8	1.10		0.13	0.28	0.48	0.32		0.062	1.0	1.7
9	---		0.25	---	---	1.86		0.71	0.060	0.098
10	0.42		0.094	0.71	1.2	0.53		0.15	0.49	0.84
11	---		0.046	---	---	2.48		0.10	0.072	0.14

Note: (1) For an assumed spill of 5000 lb. and an assumed storage temperature of 85°F, Distances are those required for concentration at center of cloud to decrease to 122.3 ppm.

(2) Determined from observed angles of cloud spread.

E. EFFECT OF REACTION WITH DRY LIMESTONE
ON CONTAMINATION DISTANCES

Of the many proposals of methods to reduce the storage hazard of liquid hydrogen fluoride, one is to store the liquid over a bed of dry limestone (calcium carbonate) to neutralize the hydrogen fluoride and thereby decrease the amount evaporated. This proposal may be evaluated by considering the effect of the heat liberated by the reaction



on the evaporation rate.

It is estimated (see Sample Calculations) that for every pound of hydrogen fluoride neutralized, 2.8 lb. of hydrogen fluoride will be vaporized due to the heat of reaction alone.

The effect of this additional vaporization on the contamination distance may be estimated. The assumptions made in the previous section are again made, and an additional assumption is that the reaction proceeds so rapidly that the resulting vapor combines with that from flashing to increase the size of the initial and instantaneous cloud.

On this basis, the amount W of hydrogen fluoride in the initial cloud is (see Sample Calculations in Appendix):

$$W = 0.74(1 + 0.35k)M \quad (21)$$

For a spill of 5000 lb. of liquid hydrogen fluoride, and for the assumed conditions, the distance x_{f+r} for the cloud concentration to decrease to 122.3 ppm. is obtained by substituting the appropriate values in equation (11):

$$x_{f+r} = \left[\frac{1.71 \times 10^6}{C_x C_y C_z} \right]^{2/3(2-n)} \quad (22)$$

The predicted distances, assuming the same values of diffusion coefficients mentioned in the previous section, are presented in Table IV.

It is clear that dry limestone increases the hazard from a hydrogen fluoride spill. Its use is not recommended.

F. PRACTICAL APPLICATION OF RESULTS

These results provide generalizations which should prove useful in formulating an emergency plan in the case of an accidental spill of liquid hydrogen fluoride. If wind velocity and direction are known at the point of release, the approximate angle of spread and contamination distance may be quickly estimated for a spill of given magnitude. Appropriate values of diffusion coefficients to be used may be estimated from those given in Tables I and II. Those values given for lapse apply on clear sunny days, and those given for inversion apply during the night and during a heavy overcast.

These generalizations can be applied quantitatively to the release of other chemicals if the toxic concentration and amount (or rate) of release are specified.

These results provide a better understanding of the requirements for safe storage of hydrogen fluoride, and lead to specific proposals for methods of reducing the hazard from an accidental spill.

V. CONCLUSIONS

1. Equations developed for the spread of clouds in the lower atmosphere over level terrain can be applied to the spread of toxic gases over the K-25 area if effective values of diffusion coefficients, as presented in Tables I and II, are used.
2. Due to the effect of local cross winds, building turbulence, and large variation in wind direction in this area, the observed angles of spread may be as much as five-fold greater than the predicted angles for lapse and as much as ninety-fold greater than the predicted angles for inversion.
3. For an assumed release of 5000 lb. of liquid hydrogen fluoride, the distance required for the concentration of hydrogen fluoride to decrease to 122.3 ppm. may be on the order of 0.2 to 0.5 miles for lapse and 0.5 to 4 miles for inversion.
4. Unless the spill is extremely large and the liquid is allowed to spread freely over the ground, the main hazard is from flashing of superheated liquid hydrogen fluoride, rather than from continuous evaporation of unflashed liquid.
5. Storing liquid hydrogen fluoride over dry limestone increases the hazard from an accidental spill.

VI. RECOMMENDATIONS

1. Anhydrous liquid hydrogen fluoride should be stored over an area surrounded by a dike so that spilled liquid will not spread freely over the area.
2. The storage vessel should be surrounded by water sprays of large capacity and designed to go into action immediately in case of a spill.
3. Further studies should be made of the rates of atmospheric evaporation of hydrogen fluoride under various meteorological conditions.

VII. APPENDIX

A. SAMPLE CALCULATIONS

1. Cloud Angle Predicted from Meteorological Measurements

The angle of spread α of the cloud from the source is approximated by

$$\alpha = 2 \tan^{-1} \left(\frac{1.52 C_y}{10^n} \right) \quad (14)$$

The lateral diffusion coefficient C_y is estimated by Holland as:

$$C_y = \frac{4.7^n}{(1-n)(2-n)u^n} (\tan \sigma_\theta)^2 \quad (3)$$

Equation (3) is solved quickly using nomograms supplied by Holland (5).

For Run 1, meteorological measurements at K-832 (which is near K-1132) lead to:

$$u = 1.79 \text{ m./sec.}$$

$$n = 0.26$$

$$\sigma_\theta = 48^\circ$$

Using these data,

$$C_y = 0.33.$$

Solving for α from equation (14):

$$\alpha = 30^\circ.$$

2. Calculation of Lateral Diffusion Coefficient from Measured Cloud Angle

Rewriting equation (14):

$$C_y = \frac{10^n}{1.52} \tan \frac{\alpha}{2} \quad (14a)$$

For Run 1, smoke release at K-1132:

$$n = 0.26$$

$$\alpha = 44^\circ \text{ (measured)}$$

$$\begin{aligned} C_y &= \frac{10^{0.26}}{1.52} \tan \frac{44}{2} \\ &= 0.48. \end{aligned}$$

Calculation of Evaporation Rate for a Spill of Liquid Hydrogen Fluoride:

It was found from these experiments that the surface temperature of hydrogen fluoride, evaporating from an insulated metal pan, remained constant at -8°C over a wide range of atmospheric conditions; hence, the effect of changes in vapor pressure P_v of hydrogen fluoride may be neglected. It is assumed that the product aP_v is small, so equation (9) may be written as:

$$Q = A_m(\bar{u})^{\frac{2-n}{2+n}} \quad (16)$$

Data for pan-evaporation experiments:

$$\bar{u} = 1.99 \text{ m./sec.}$$

$$n = 0.20$$

$$\text{surface area for evaporation} = 1250. \text{ sq. in.}$$

$$\text{amount HF evaporated} = 28.8 \text{ lb.}$$

$$\text{time of evaporation} = 42.0 \text{ min.}$$

$$\begin{aligned}
 m &= \left(\frac{28.8 \text{ lb.}}{42.0 \text{ min.}} \right) \left(\frac{1}{1250 \text{ sq. in.}} \right) \left(\frac{454 \text{ g.}}{\text{lb.}} \right) \left(\frac{\text{min.}}{60 \text{ sec.}} \right) \left(\frac{1550 \text{ sq. in.}}{\text{sq. m.}} \right) \\
 &\quad \left(\frac{1}{1.99} \right)^{\frac{1.8}{2.2}} \\
 &= 3.68 \text{ g./}(\text{sec.})(\text{sq. m.})(\text{m./sec.})^{\frac{2-n}{2+n}}
 \end{aligned}$$

3. Distance for Hydrogen Fluoride in Gas Cloud Resulting from Continuous Evaporation to Decrease to 122.3 ppm.

It is assumed that:

1. A spill of 5000 lb. of anhydrous liquid hydrogen fluoride occurs.
2. The unflashed liquid spreads on the ground to form a pool one inch deep.
3. The ambient temperature is 75°F (24°C).
4. The liquid hydrogen fluoride is stored at 85°F.
5. The steady-state surface temperature of the spilled liquid is 17.6°F (-8°C).

From reference (4) the vapor pressure for hydrogen fluoride at -8°C is:

$$P_v = 5 \text{ lb./sq. in. (absolute).}$$

The gas concentration χ_0 at the point of release is:

$$\begin{aligned}
 \chi_0 &= \left(\frac{\text{mole}}{22.4 \text{ liters}} \right) \left(\frac{273}{297} \right) \left(\frac{5 \text{ moles HF}}{14.7 \text{ moles total}} \right) \left(\frac{20 \text{ g. HF}}{\text{mole HF}} \right) \left(\frac{1000 \text{ liters}}{\text{cu. m.}} \right) \\
 &= 279 \text{ g. HF/cu. m.}
 \end{aligned}$$

The gas concentration χ_t corresponding to 122.3 ppm. is:

$$\begin{aligned}
 \chi_t &= \left(\frac{122.3 \text{ moles HF}}{10^6 \text{ moles air}} \right) \left(\frac{20 \text{ g. HF}}{\text{mole HF}} \right) \left(\frac{\text{mole}}{22.4 \text{ liters}} \right) \left(\frac{273}{297} \right) \left(\frac{1000 \text{ liters}}{\text{cu. m.}} \right) \\
 &= 0.1005 \text{ g. HF/cu. m.}
 \end{aligned}$$

From reference (4),

$$H_{L1} = 10 \text{ B.t.u./lb.}$$

$$H_{L2} = 0 \text{ B.t.u./lb.}$$

$$\Delta H_V = 173 \text{ B.t.u./lb.}$$

$$\begin{aligned} \rho_L &= (8.51 \text{ lb./gal.})(454 \text{ g./lb.})(\text{gal./}0.003785 \text{ cu. m.}) \\ &= 1.021 \times 10^6 \text{ g./cu. m.} \end{aligned}$$

$$\begin{aligned} k &= \frac{H_{L1} - H_{L2}}{\Delta H_{V2} - H_{L2}} = \frac{10}{173} \\ &= 0.0576 \text{ lb. flash/lb. spilled.} \end{aligned}$$

surface area:

$$\begin{aligned} &= \frac{(5000 \text{ lb.})(1 - 0.0576)}{(8.51 \text{ lb./gal.})(7.48 \text{ gal./cu. ft.})(1/12 \text{ ft.})} \\ &= 888 \text{ sq. ft.} \\ A &= (888 \text{ sq. ft.})(0.0929 \text{ sq. m./sq. ft.}) \\ &= 82.5 \text{ sq. m.} \end{aligned}$$

Equation (18) becomes

$$\begin{aligned} x_c &= \left\{ \left[\frac{(2)(82.5)(3.68)}{\pi C_y C_z} \right]^{\frac{1}{2-n}} \left[\left(\frac{1}{0.1005} \right)^{\frac{1}{2-n}} - \left(\frac{1}{279} \right)^{\frac{1}{2-n}} \right] \left(\frac{1}{u} \right)^{\frac{2n}{4-n^2}} \right\} \\ &= \left[\frac{1933}{C_y C_z} \right]^{\frac{1}{2-n}} \left(\frac{1}{u} \right)^{\frac{2n}{4-n^2}} \end{aligned}$$

a. Assume isotropic turbulence:

For Run 1, K-832 (near K-1132)

$$\bar{u} = 1.79 \text{ m./sec.}$$

$$n = 0.26$$

$$C_y = C_z = 0.33$$

$$x_c = \left[\frac{1933}{(0.33)^2} \right]^{\frac{1}{1.74}} \left(\frac{1}{1.79} \right)^{\frac{0.52}{3.93}}$$

$$= 241 \text{ m.}$$

$$(241 \text{ m.})(0.000621 \text{ miles/m.}):$$

$$= 0.149 \text{ miles}$$

From equation (17):

$$\text{rate of evaporation} = (82.5)(3.68)(1.79)^{\frac{1.74}{2.26}}$$

$$= 475 \text{ g./sec.}$$

$$(475 \text{ g./sec.})(\text{lb./454 g.})(60 \text{ sec./min.}) = 62.8 \text{ lb./min.}$$

$$\text{evaporation time} = \left[\frac{(5000)(1 - 0.0576)\text{lb.}}{62.8 \text{ lb./min.}} \right] (\text{hr./60 min.})$$

$$= 1.2 \text{ hr.}$$

b. Assume anisotropic turbulence:

For Run 1, K-832 (near K-1132)

$$\bar{u} = 1.79 \text{ m./sec.}$$

$$n = 0.26$$

$$C_z = 0.33$$

$$C_y = 0.48 \text{ (from observed cloud angle)}$$

$$x_c = 195 \text{ m., or } 0.1207 \text{ miles}$$

4. Contamination Distances Resulting from Flash of Spilled Liquid

The assumptions described under (3) are also used here. An additional assumption is that the center of the cloud formed almost instantaneously consists of pure hydrogen fluoride at 75°F.

From reference (4), density of saturated HF vapor at 75°F:

$$= 0.180 \text{ lb./cu. ft.}$$

$$\begin{aligned} \chi_o &= (0.180 \text{ lb./cu. ft.})(454 \text{ g./lb.})(\text{cu. ft.}/0.0283 \text{ cu. m.}) \\ &= 2890 \text{ g./cu. m.} \end{aligned}$$

Amount flashed,

$$\begin{aligned} W &= \text{kM} \\ &= (0.0576 \text{ lb/lb.})(5000 \text{ lb.})(454 \text{ g./lb.}) \\ &= 1.31 \times 10^5 \text{ g.} \end{aligned}$$

Substituting values in equation (11):

$$\begin{aligned} x_f &= \left[\frac{(2)(1.31 \times 10^5)}{\pi^{3/2} c_x c_y c_z} \right]^{\frac{2}{3(2-n)}} \left[\left(\frac{1}{0.1005} \right)^{\frac{2}{3(2-n)}} - \left(\frac{1}{2890} \right)^{\frac{2}{3(2-n)}} \right] \\ &= \left(\frac{4.66 \times 10^5}{c_x c_y c_z} \right)^{\frac{2}{3(2-n)}} \end{aligned}$$

For Run 1, K-832 and K-1132, and assuming isotropic turbulence in the horizontal plane only:

$$n = 0.26$$

$$c_x = c_y = 0.48 \text{ (from observed angles)}$$

$$c_z = 0.33 \text{ (from meteorological measurements)}$$

$$x_f = \left[\frac{466 \times 10^5}{(0.048)(0.048)(0.33)} \right]^{\frac{2}{3(1.74)}} = 390 \text{ m.}$$

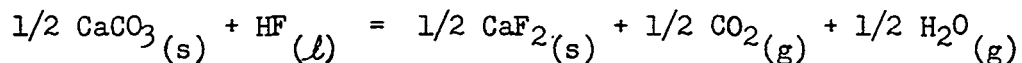
$$(390)(0.000621) = 0.24 \text{ miles}$$

Effect of Reaction of Hydrogen Fluoride with Dry Calcium Carbonate

The same assumptions as made in the previous sections apply here. Also, it is assumed that:

- a. That portion of the spill which does not flash reaches the calcium carbonate instantaneously. Sufficient hydrogen fluoride reacts so that the heat of reaction is just sufficient to vaporize the unreacted hydrogen fluoride.
- b. That portion of the hydrogen fluoride vaporized due to heat of reaction combines with that vaporized due to flashing, and a cloud forms almost instantaneously.
- c. The water from the chemical reaction comes off as a vapor. This neglects the probable dilution of the liquid hydrogen fluoride due to condensed moisture.

For the reaction



the following heats of formation are obtained (6):

<u>Compound</u>	<u>Heat of Formation at 18°C</u>
	Kcal./g. mole
CaCO ₃	- 289.3
CaF ₂	- 290.2
CO ₂	- 94.03
HF(l)	- 71.0
H ₂ O(g)	- 57.8

The heat of reaction (1) at 18°C is:

$$\begin{aligned} & 1/2 \left[-290.2 - 94.03 - 57.8 + 289.3 + 2(71.0) \right] \\ & = 5.36 \text{ Kcal./g. mole of HF reacted.} \end{aligned}$$

$$\begin{aligned} \Delta H_R & = (5360)(1.8)(1/20) \\ & = 482 \text{ B.t.u./lb. HF reacted.} \end{aligned}$$

The latent heat of vaporization (4, 9) of hydrogen fluoride at 19.5°C (67°F) is:

$$\Delta H_{V_2} = 173 \text{ B.t.u./lb.}$$

For each lb. of hydrogen fluoride reacted, the heat of reaction is sufficient to vaporize $\Delta H_R / \Delta H_V$ lb. of hydrogen fluoride.

$$\begin{aligned} \frac{\Delta H_R}{\Delta H_V} & = \frac{5.36}{1.923} \\ & = 2.79 \text{ lb. HF vaporized/lb. HF reacted.} \end{aligned}$$

Total amount in initial cloud:

$$\begin{aligned} & = \text{amount flashed} \\ & + \text{amount vaporized from heat of reaction.} \end{aligned}$$

$$\begin{aligned} W & = kM + (1 - k) \left(\frac{2.79}{3.79} \right) M \\ & = \left[0.0576 + (0.942) \left(\frac{2.79}{3.79} \right) \right] (5000)(454) \\ & = 1.708 \times 10^6 \text{ g.} \end{aligned}$$

Equation (11) becomes:

$$x_f = \left[\frac{1.708 \times 10^6}{C_x C_y C_z} \right]^{\frac{2}{3(2-n)}}$$

For Run 1, K-832 and K-1132,

$$\bar{u} = 0.26$$

$$C_x = C_y = 0.48$$

$$C_z = 0.33$$

$$x_{f+r} = \left[\frac{1.708 \times 10^6}{(0.48)(0.48)(0.33)} \right]^{\frac{2}{3(1.67)}}$$

$$= 640 \text{ m.}$$

$$(640)(0.000621)$$

$$= 0.40 \text{ miles}$$

B. TABLE OF NOMENCLATURE

a	constant in equation (10).
A	surface area of evaporation, sq. m.
b	constant in equation (9).
C_x	diffusion coefficient in mean wind direction, (m.) ⁿ .
C_y	lateral diffusion coefficient, (m.) ⁿ .
C_z	vertical diffusion coefficient, (m.) ⁿ .
h	depth of pool of spilled liquid, m.
H_{L1}	enthalpy of stored liquid, B.t.u./lb.
H_{L2}	enthalpy of saturated liquid at atmospheric pressure, B.t.u./lb.
k	ratio of liquid flashed to liquid spilled, g./g.
m	constant in equation (17), g./((sec.)(sq. m.)(m./sec.) ^{$\frac{2-n}{2+n}$}).
M	total amount spilled, g.
n	atmospheric stability term.
P_v	vapor pressure of evaporating liquid, lb./sq. in. (absolute).
Q	rate of generation of gas or smoke, g./sec.
r	radius of puff, m.
t	time elapsed after instantaneous release, sec.
u	instantaneous downwind component of wind velocity, m./sec.
\bar{u}	mean wind velocity, m./sec.
	\bar{u}_1 and \bar{u}_2 are mean wind velocities at elevations of z_1 and z_2 .
v'	instantaneous crosswind component of wind velocity, m./sec.
w'	instantaneous vertical component of wind velocity, m./sec.
W	amount of gas released instantaneously, g.

x	downwind distance from source, m.
x_c	downwind distance from point of release for concentration in cloud resulting from continuous release to decrease to χ_t , m.
x_f	downwind distance from point of release for concentration in cloud resulting from flash to decrease to χ_t , m.
x_{f+r}	downwind distance from point of release for concentration in cloud resulting from flash and chemical reaction to decrease to χ_t , m.
x_0	fictitious distance upwind from point of release to virtual point source where cloud concentration is infinite, m.
y	crosswind distance from source, measured horizontally and perpendicular to x axis, m.
y_0	crosswind distance at which ground-level concentration is one-tenth that directly downwind of source, m.
y_c	crosswind distance to cloud boundary at ground level, m.
z	elevation above ground, m.
	z_1 and z_2 refer to elevations at which wind velocity is measured.
α	mean angle of spread from point of release, degrees.
χ	concentration of diffusing component, g./cu. m.
χ_0	cloud concentration immediately above point of release, g./cu. m.
χ_t	concentration at boundary of area of contamination, g./cu. m.
ΔH_R	heat released from reaction (21), B.t.u./lb. HF.
ΔH_{V2}	latent heat of vaporization, B.t.u./lb. from saturated liquid at atmospheric pressure.
ν	kinematic viscosity of air, sq. m./sec.
ρ_L	density of spilled liquid, g./cu. m.
σ_θ	standard deviation of instantaneous angular deviation of wind from mean direction, degrees.

C. LITERATURE CITATIONS

1. Atomic Energy Commission, "Handbook on Aerosols", Washington, D. C. (1950).
2. Bahler, K. W., Private Communication, K-25 Plant, Oak Ridge (1951).
3. Calder, K. L., "The Diffusive Properties of the Lower Atmosphere", No. 9.401, Ministry of Supply, London (1948).
4. Carbide and Carbon Chemicals Company, Technical Data Book II, A-4739 (1947).
5. Holland, J. Z., Private Communication, U. S. Weather Bureau, Oak Ridge (1951).
6. Hougen, O. A., and Watson, K. M., "Chemical Process Principles", 1st. ed., Pts. I and II, John Wiley & Sons, New York (1947).
7. Myers, R. F., "Meteorological Instruments in Use by the Meteorological Survey", U. S. Weather Bureau, Oak Ridge (1951).
8. Newton, H., et al., A.E.C. Meteorological Information Meeting, TID-399 (1951).
9. Othmer, D. F., and Kirk, R. E., "Encyclopedia of Chemical Technology", 6, The Interscience Encyclopedia, Inc., New York (1951).
10. Sutton, O. G., Quarterly Journal of the Royal Meteorological Society, 73, 257-281 (1947).

~~SECRET~~
SECURITY INFORMATION

51

D. ACKNOWLEDGEMENTS

The original data presented herein were obtained by M.I.T. Practice School students C. B. Beck, T. D. Canby, and I. S. Zonis. Considerable help in carrying out this work, as well as in the interpretation of results, was supplied by:

J. Z. Holland and R. F. Myers of the U. S. Weather Bureau, Oak Ridge.

K. W. Bahler and K. P. Moseley of the K-25 Safety and Protection Division.

S. Henck of the Atomic Energy Commission, Oak Ridge.

Captain Noel and Sergeant Harpin of the U. S. Air Force, Wright Field.

E. Halterman and H. D. Phillips of the K-25 Plant Protection Division.

~~SECRET~~
SECURITY INFORMATION